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Iron biogeochemistry across marine systems – progress from the past decade

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Abstract. Based on an international workshop (Gothenburg, 14–16 May 2008), this review article aims to combine interdisciplinary knowledge from coastal and open ocean research on iron biogeochemistry. The major scientific findings of the past decade are structured into sections on natural and artificial iron fertilization, iron inputs into coastal and estuarine systems, colloidal iron and organic matter, and biological processes. Potential effects of global climate change, particularly ocean acidification, on iron biogeochemistry are discussed. The findings are synthesized into recommendations for future research areas.

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1 Preface

An international workshop addressing the biogeochemistry of iron in the context of global change across marine ecosystems was held in Gothenburg, Sweden (14–16 May 2008). Largely driven by geographic separation, iron biogeochemistry in the open ocean and in coastal seas are often addressed as two distinct fields and the workshops organized over the past two decades have normally either been system- or task-specific. This has led to the development of system-specific expertise and research approaches, with potential separation of know-how. The aim of this workshop was to conduct a broader cross-system review of marine iron biogeochemistry by bringing together scientists from a wide range of coastal, shelf and deep-ocean environments to merge their system-specific knowledge into a truly cross-disciplinary and cross-system synthesis. This lead article is an attempt to

summarize the scientific milestones of the past 10 years discussed during the workshop.

The Gothenburg workshop was convened almost ten years after a workshop meeting in Amsterdam, sponsored by SCOR and IUPAC which formed the basis for the book "The Biogeochemistry of Iron in Seawater" (Turner and Hunter, 2001). The Gothenburg workshop revisited the topics listed in the "Summary and Recommendations" of this book and took up two further cross-cutting aspects: (A) What can we learn from comparing Fe biogeochemistry in coastal and open ocean systems? And (B), how are global change processes expected to affect Fe biogeochemistry?

This article aims to synthesize the cross-system and interdisciplinary knowledge from atmospheric, chemical, biological, and geological angles discussed during the Gothenburg workshop and ties the manuscripts of the special issue "Iron biogeochemistry across marine systems at changing times" into this overall context. Due to this wide range of topics, it is not intended to be a comprehensive, in-depth review on all aspects of marine iron biogeochemistry. We follow the structure of the workshop topics, which were: Natural Fe fertilization (Sect. 2, articles: Ardelan et al., 2010; Chever et al., 2010; Duggen et al., 2010; Ye et al., 2009); artificial Fe fertilization (3: Bucciarelli et al., 2010; Chever et al., 2010); Fe inputs into coastal and estuarine systems (4: Gelting et al., 2009; Breitbarth et al., 2009); Colloidal iron and organic matter (5); Linking biological processes to iron chemistry (6: Breitbarth et al., 2009; Bucciarelli et al., 2010; Hassler and Schoemann, 2009; Steigenberger et al., 2010); and Iron and Climate Change (7: Breitbarth et al., 2010; Rose et al., 2009). Each section concludes with recommendations for future research.

2 Natural iron fertilization

The past decade brought major advances in the understanding of natural iron fertilization processes to the open ocean. The field is generally subdivided into two major areas: atmospheric deposition with the main focus on dust deposition from the continents and more recently addressing volcanic ash and pumice depositions; and marine processes, where particular areas of interest have been ice melting, hydrothermal vents, continental margins, and the island mass effects.

2.1 Atmospheric deposition – dust

Over the last 10 years, the importance of dust transport and deposition within the Earth System has become clear (Jickells et al., 2005). This includes the role of dust in transporting iron to the oceans, but also the transport of nutrients to land and impacts on albedo. Dust supply is episodic and predominantly from desert regions, and satellite advances have allowed these sources to be better characterized (Prospero et al., 2002). These satellite advances also allow some improvement in understanding of dust transport and deposition, but this is still limited to high dust regions where the total aerosol is dominated by dust (Mahowald et al., 2005). In regions remote from the desert sources, aerosols may be dominated by sea and acid salts. Furthermore close to a source region, particularly over the ocean off North Africa, the dust is transported at altitude, so the satellite detection of a dust plume, does not necessarily imply deposition to the oceans at that location (Mahowald et al., 2005). Since dust transport is episodic, field data to validate models and provide direct estimates of dust loading should ideally cover periods of months to years. Obviously though, shorter campaign style measurements can be useful for studying processes, and if repeated can provide long term average concentrations. The number of long-term dust monitoring stations is still very limited and broadly the same as identified in Jickells and Spokes (2001). This data set is dominated by the Prospero network (e.g. Ginoux et al., 2004), and the lack of data in the low dust regions, where ocean euphotic zone iron limitation is evident, is notable. Recent campaigns in some of these regions (Baker et al., 2006; Planquette et al., 2007; Wagener et al., 2008) do provide some confidence in the dust transport models, but the uncertainties in parameterizations within the models are still considerable and hence the uncertainties in flux estimates are still substantial. The work of Measures and colleagues (e.g. Han et al., 2008) has demonstrated the validity of a novel indirect approach of using surface water Al as a tracer of atmospheric deposition which provides data averaged over long time scales (months to years) in remote regions. Again this approach has significant uncertainties, but the broad agreement between this, long term field data, campaign data and models provides reassurance that the estimates of total dust deposition to the oceans and the regional patterns are realistic.

A major continuing source of uncertainty in estimating dust deposition to the oceans is associated with the parameterisation of wet and dry deposition, except in the few cases where wet deposition has been measured directly. The congruence of data and models noted above does provide some confidence that, at the global scale, the average deposition parameterization is approximately correct. This does not mean that the resultant dust flux from these averages is estimated correctly at the regional scale, or in the low dust regions of water column iron limitation. Duce et al. (1991) estimated uncertainties of a factor of three in the deposition flux and this uncertainty largely remains. Jickells et al. (1998) demonstrated that the use of ocean sediment trap data can provide a valuable constraint on the uncertainties in deposition fluxes and Mahowald et al. (2005) considered this further. However, the use of this technique in low dust regions does require high quality measurements of a dust tracer such as Al in the sediment traps and this is not always available. If this became routine it would offer a mechanism to significantly reduce uncertainties in deposition parameterization. Such an improvement would allow dust and iron mass

balance in individual regions and comparison to productivity estimates.

The conversion of dust deposition to soluble iron fluxes requires the solubility of iron from dust to be known. This is required ideally over the timescale of the residence times of dust in the water column (tens of days, see Jickells et al., 2005) and at realistically low dust loadings, although this is very difficult in practice and more pragmatic short term simple aerosol leaching schemes are usually applied (Baker and Croot, 2009).

Considerable effort has been put into studies of aerosol dust solubility over the last 10 years and this has tended to confirm that on a global average Fe solubility is low (Jickells et al., 2005; Mahowald et al., 2005), but also demonstrated that the use of a single solubility estimate is probably inappropriate and there does appear to be a systematic increase in solubility from high to low dust regions (Baker and Croot, 2009; Baker and Jickells, 2006). There is still considerable debate surrounding the drivers of this variation in solubility with four main possibilities; (i) atmospheric chemical processing during dust transport (Fan et al., 2006; Jickells and Spokes, 2001), (ii) systematic changes in aerosol particle size leading to changes in surface area and solubility (Baker and Jickells, 2006), (iii) an additional source of iron beside crustal dust (Jickells et al., 2005; Schroth et al., 2009); (iv) active biological acquisition and uptake mechanisms such as siderophores and grazing that can circumvent abiotic dissolution limitations (Barbeau and Moffett, 2000; Yoshida et al., 2002; Frew et al., 2006).

There is good evidence that solubility of iron from anthropogenic aerosol is higher than from soil dust (Schroth et al., 2009; Journet et al., 2008) but the significance of this high solubility anthropogenic dust to the global iron cycle is uncertain, and in particular it seems unlikely to be responsible for high iron solubilities in aerosols in remote regions seen for instance by Baker and Jickells (2006). However, recent measurements of iron speciation from African dust collected in the Trade Winds at Barbados support the case for anthropogenic iron controls over iron solubility. Trapp et al. (2010) show that Fe^{3+} dominates the iron solubility over the entire range of particle sizes. However, at low mineral dust concentrations Fe^{2+}, believed to be largely derived from anthropogenic sources, becomes increasingly important. Airmass back trajectories indicate biomass burning in southern Africa and potentially also South America as the source of this anthropogenic iron and dust samples had an Fe^{2+}/Fe^{3+} ratio twice that measured in dust-laden aerosols from North Africa. (Trapp et al., 2010).

In their contribution to this special issue, Ye et al. (2009) aim to improve the understanding of the impact of dust deposition on Fe bioavailability and marine primary productivity in modeling iron speciation and biogeochemistry at TENATSO (Tropical Eastern North Atlantic Time-series Observatory). Based on recent studies on Fe speciation and the existing model for the Bermuda Atlantic Time-series Study (BATS) (Weber et al., 2007), this model aims at studying the role of dust particles in Fe removal and providing a better description of the sources and fate of organic Fe-binding ligands.

Dry deposition probably dominates dust and iron deposition over some regions of the ocean, particularly those where winds flow off the land including areas downwind of major deserts such as the Sahara. Wet deposition is probably particularly important for total deposition in remote regions of the ocean. The data set for dust and soluble iron in wet deposition in the marine atmosphere is very small, and this requires improvement. To date, this discussion has largely considered only dust and iron deposition. However, atmospheric deposition delivers significant amounts of iron (Jickells et al., 2005) and nitrogen (Duce et al., 2008) and relatively small amounts of phosphorus (Mahowald et al., 2008) relative to phytoplankton requirements. Assorted trace metals that may play a role in phytoplankton productivity, including some that are potentially inhibitory, will also be deposited (e.g. Paytan et al., 2009). It is important that we evaluate the impacts of atmospheric deposition holistically, and not artificially separate the contributions of individual nutrients.

2.2 Other atmospheric and marine processes of natural Fe fertilization

All short-term artificial Fe fertilization experiments unequivocally showed the importance of Fe on the carbon cycle, in particular on the food web structure and functioning (e.g. Boyd, 2004; Boyd et al., 2007, 2000; Coale et al., 1996, 2004; Gervais et al., 2002; Tsuda et al., 2003; de Baar et al., 2005, see Sect. 2). However, it is difficult to reliably assess the magnitude of carbon export to the ocean interior using such methods (Blain et al., 2007). Recent natural Fe fertilization experiments carried out in the Southern Ocean showed that the efficiency of fertilization was at least 10 to 20 times greater than that of a phytoplankton bloom induced artificially by adding iron, (KEOPS and CROZEX, Blain et al., 2007; Pollard et al., 2009). Large losses of purposefully added iron can explain the lower efficiency of the induced bloom, as well as the mode of iron addition and the requirement of concomitant supply with major nutrients (Pollard et al., 2009; Blain et al., 2007). In the open ocean, a large variety of naturally iron-fertilized sites exist, which could allow for improved forecasting of the oceanic response to Fe fertilization and a better knowledge of Fe sources to the open ocean. Chever et al. (2010) provide a Fe budget for the naturally fertilized area above the Kerguelen Plateau, using total dissolvable Fe as an additional tracer to better constrain the Fe cycle in this area. They show that horizontal advection of water from South of the Plateau seems to be the predominant source of apparent particulate and dissolved iron above the plateau, over atmospheric and vertical inputs. Further, Ardelan et al. (2010) illustrate natural Fe enrichment processes from the South Shetland Islands-Antarctic Peninsula region.

As discussed in Sect. 2.1, aeolian inputs may have different origins, such as (i) the arid and semi-arid regions (Jickells et al., 2005), (ii) combustion sources (fossil fuel burning, incinerator use, biomass burning; (Spokes and Jickells, 2002; Guieu et al., 2005; Sedwick et al., 2007; Luo et al., 2008), but also by (iii) meteoritic material and extraterrestrial dust (Johnson, 2001), and (iv) volcanic origin (Benitez-Nelson et al., 2003; Duggen et al., 2007; Boyd et al., 1998). All atmospheric input may have an effect on biological productivity in the ocean (Schroth et al., 2009), in particular on bacterial activity (Pulido-Villena et al., 2008), although the causative link is not always obvious as shown by (Boyd et al., 2009).

While the meteoritic contribution is difficult to assess due to the sporadic events, the amount of soluble (presumably bioavailable) iron input into the ocean from extraterrestrial dust is estimated to be $7\times109\,\mathrm{g\,year^{-1}}$ (Johnson, 2001) and is thus not insignificant. More so, volcanic eruptions can transport volcanic ash up to several tens of kilometres high into the atmosphere and fine ash may encircle the globe for years, thereby reaching even the remotest and most iron-starved oceanic areas (Schmincke, 2004). The implication of volcanism for the marine biogeochemical iron-cycle is poorly constrained so far. Recent studies demonstrate that volcanic ash from volcanoes worldwide quickly releases soluble and bio-available iron on contact with water (e.g. Jones and Gislason, 2008; Duggen et al., 2007; Frogner et al., 2001). Drill core data from scientific ocean drilling show that volcanic ash layers and dispersed ash particles are frequently found in marine sediments and that volcanic ash deposition and therefore iron-injection into the oceans took place throughout much of the Earths history (Straub and Schmincke, 1998). It may thus well be possible that the contribution of volcanic ash to the marine biogeochemical iron-cycle is generally underestimated. A review paper (Duggen et al., 2010) summarises the development and the knowledge in a fairly young research field covering a wide range of chemical and biological issues and gives recommendations for future directions. The approach by Duggen et al. (2010) contributes to understanding of the role of volcanic ash for the marine biogeochemical iron-cycle, marine primary productivity and the ocean-atmosphere exchange of CO_2 and other gases relevant for climate throughout the Earths' history.

Melting of sea ice, icebergs and glacial inputs may contribute as Fe sources in polar regions. Estimates of these sources' magnitudes are poorly constraint. Recent studies have highlighted the importance of these sources (Lannuzel et al., 2008; Lannuzel et al., 2007; Statham et al., 2008; Aguilar-Islas et al., 2008; Raiswell et al., 2008, 2006; Smith et al., 2007; Croot et al., 2004). Iron accumulates in sea ice with concentrations one to two orders of magnitude higher than the underlying seawater. Atmospheric iron can be one source but flux estimates by Lannuzel et al. (2008, 2007) seem to indicate that iron must come mostly from below. The exact mechanism remains unclear, but recent evidence suggests that organic matter could play an essential role in trapping Fe in the sea ice not only during sea ice formation but also during ice algae proliferation in the bottom ice after its formation (Schoemann et al., 2008). Its release into the seawater during ice melting can occur in short time spans such as weeks. For example, Lannuzel et al. (2008) showed that 70% of the accumulated Fe in the sea ice could be released due to brine drainage in a 10 days period, while the sea ice cover was still present. This represents a significant Fe flux to the surface ocean that may be instrumental in sustaining springtime ice edge blooms in the marginal ice zone and polynias. Dense phytoplankton blooms have been observed in combination with the receding ice edge or in coastal shelf areas (e.g. Smith and Nelson, 1985; Holm-Hansen et al., 1989). Moreover, both sea ice and icebergs may constitute vectors of Fe transport far away from its initial source (Smith et al., 2007; Lancelot et al., 2009). Further to this, Edwards and Sedwick (2001) addressed the contribution of snow bound aerosol iron in the Antarctic seasonal sea ice zone.

The continental margins may also play a key role as a Fe source (Elrod et al., 2004; Laës et al., 2003, 2007; Chase et al., 2005; Blain et al., 2008). As an example, Lam and Bishop (2008) clearly showed that the continental margin was a key source of Fe to the HNLC (high nutrient low chlorophyll) North Pacific Ocean, since the lateral source of Fe is shallow enough to be accessible to phytoplankton by winter mixing and Fe can be transported at distance over 900 km from the continental shelf.

Our current challenge in regions where natural iron fertilization occurs is to have a better knowledge and quantification of these various Fe sources. For example, the global atmospheric iron fluxes are reasonably well known, but the fluxes to remote low iron regions are rather uncertain. Moreover, the aerosol iron solubility varies systematically, but the underlying causes of this are uncertain. In the deep waters, Fe can be transported far away from the source, especially in waters with anoxic conditions (Blain et al., 2008). Local and remote sources of Fe may not have the same impact on carbon cycle. We also need to understand how (i) the different sources of Fe influence its speciation and bioavailability; (ii) they contribute to the global Fe budget; (iii) they will be affected by global change, and (iv) what are the physical mechanisms that allow long distance Fe transport: advection (strong currents, ACC, EUC, de Baar et al., 1995; Mackey et al., 2002; Lam and Bishop, 2008; Loscher et al., 1997), internal waves and slope circulation (Laës et al., 2003), and eddies (Johnson et al., 2005). Finally, the physical mechanisms that allow Fe to be accessible for the food web should also be better understood and quantified (upwelling, diapycnal mixing, winter mixing, Blain et al., 2007).

To asses these challenging issues, there is a crucial need for (i) multi-disciplinary studies (physics/biogeochemistry/biology), (ii) multi-proxy approaches, such as the one promoted by the international

GEOTRACES program, including oceanic sections and intercalibration experiments for seawater and aerosols; (iii) the development of biogeochemical models that correctly take into account the various Fe sources and their impact on Fe speciation and bioavailability, and (iv) the development of regional iron budgets.

3 Artificial iron fertilization

The largest source of iron for the HNLC surface waters comes from deep water supply (Watson, 2001). However, the Fe:N or Fe:P ratio of the upwelled deep waters is often not high enough for optimum phytoplankton growth (Moore et al., 2006). Consequently, an additional source of iron is required, which could be derived from suboxic or anoxic sediments (Las et al., 2007) or dust inputs (Jickells et al., 2005). Fertilization of the Southern Ocean with dust has been suggested as an explanation for past glacial periods (Martin, 1990). During these periods iron dust inputs to the oceans were strongly enhanced, with the Southern Ocean receiving up to 10 times more dust-derived iron (Wolff et al., 2006), and consequent stimulation of phytoplankton growth and the biological carbon pump. Nevertheless, it has been estimated that the increase in iron stimulated productivity could have contributed perhaps 15–25% of the 80–100 ppm drawdown in atmospheric CO_2 observed during glacial maxima by enhancing the biological carbon pump (Sigman and Boyle, 2000; Bopp et al., 2003).

When trace metal clean techniques became available in the late 1980s it was possible to directly test the effect of iron additions on phytoplankton growth in HNLC regions. Ship-board iron-addition bottle experiments clearly showed that these additions stimulated phytoplankton growth (e.g. de Baar et al., 1990). However, the potential for bottle-effects during these experiments led researchers to plan and undertake mesoscale Lagrangian-type oceanic experiments to study the influence of iron additions on primary productivity, and investigate the consequences for nutrient utilization, ecosystem dynamics and carbon export. More than a dozen of these large scale (typically 10×10 km grid) iron addition experiments have been conducted to date in HNLC regions and were reviewed by de Baar et al. (2005) and Boyd et al. (2007). Recent experiments involved conducting iron, carbon, nutrient, climatically active gasses, and ecosystem observations, the latest being Lohafex (January–March, 2009; Editorial Nature Geoscience, Editorial, 2009) following a 300 km^2 iron addition in a stable Southern Ocean mesoscale eddy for >7 weeks. The longer time scale allowed a thorough examination of biogeochemical and ecosystem changes and carbon export.

In summary, all artificial iron experiments have confirmed that iron supply limits primary production and has impact on phytoplankton species composition and bloom dynamics in tropical as well as in polar HNLC waters (Boyd et al., 2007; de Baar et al., 2005). Iron limitation also induces a decoupling in the use of macronutrients by phytoplankton, likely to influence the cycling of the major biogeochemical cycles (C, N, P, Si, S) over geological time scales (de Baar and La Roche, 2003). In addition to iron, light has been shown to play an important role in the regulation of phytoplankton production in HNLC regions (Moore et al., 2007a, b; Maldonado et al., 1999; Boyd et al., 2001; Hoffmann et al., 2008; de Baar et al., 2005; Bucciarelli et al., 2010). Overall, in situ iron fertilization experiments have greatly enhanced our knowledge about iron solubility, organic iron complexation, and the importance of iron redox states (e.g. Rue and Bruland, 1995; Croot et al., 2001; Rue and Bruland, 1997), which apply to Fe biogeochemistry in the ocean in general.

Large scale iron oceanic addition has been suggested as an option for mitigating the present day increasing atmospheric CO_2 concentrations (Kintisch, 2007). The Southern Ocean is the HNLC region where iron stimulation of CO_2 sequestration would be most efficient and yield long-term carbon storage in deeper waters (Sarmiento and Orr, 1991). Currently there are a number of uncertainties surrounding intentional, large-scale, ocean iron fertilization, which will require further research for clarification. These have already been critically assessed by Chisholm et al. (2001) as well as more recently by Buesseler et al. (2008). Potential side effects include that the mineralization of the enhanced sinking phytoplankton biomass could result in local anoxia and consequent negative effects to oceanic ecosystems and the production of the harmful greenhouse gases nitrous oxide and methane (Cullen and Boyd, 2008; Furman and Capone, 1991). Other climate active gases, like dimethylsufide (DMS) might increase following Fe fertilisation (Liss et al., 2005). Direct ecosystem shifts resulting in for example proliferation of jellyfish have also been suggested. Furthermore, purposeful iron fertilization may result in a reduced nutrient inventory and consequently reduced productivity and potentially fisheries in oceanic systems downstream of the fertilization areas (Gnanadesikan et al., 2003).

A further key unknown is the efficiency of carbon removal. The amount of carbon sequestered per unit addition of iron is crucial to the effectiveness of iron fertilization (de Baar et al., 2008). The artificial experiments have indicated an efficiency of biological carbon export into deeper water (100–250 m) ranging from 650 (SERIES, Boyd et al., 2004) to 3300 (mol C/mol Fe) (SOFEX – south, Buesseler et al., 2004). The seasonal sequestration efficiencies estimated for natural Fe fertilization are much higher, 8640 for CROZEX (Pollard et al., 2009) and 154 000 for KEOPS (Chever et al., 2010). The discrepancies in effectiveness between natural and purposeful fertilizations might be partly due to the $\sim$75% immediate loss of added Fe in artificial fertilisations (de Baar et al., 2008). These values will need to be much more tightly constrained to allow a thorough assessment of the potential success of iron fertilization as a means to reduce the increasing atmospheric CO_2 concentrations and cost

(Boyd, 2008). The success of the large scale oceanic additions of iron has furthermore been put into doubt by modeling studies. Recent work by Dutkiewicz et al. (2005) and Aumont and Bopp (2006) suggests that large scale iron additions would only reduce atmospheric CO_2 concentrations by ca. 10 ppm, as other limiting factors such as light and zooplankton grazing become more important. It appears that large uncertainties remain with respect to the efficiency of iron fertilization that require further investigations using observation and models. For a recent in depth assessment of the topic see Boyd et al. (2007), as well as Boyd (2008) and associated publications. From a marine trace-metal research perspective, the attendants of the workshop came to the conclusion, that priority should be given to small scale open ocean Fe biogeochemistry studies that are specifically designed to address clearly defined research questions of trace-metal chemistry.

4 Fe inputs into coastal and estuarine systems

The coastal area is a key environment in the global iron cycle, where the brackish water environment changes the physicochemical speciation, and thus mobility, of river-introduced iron via aggregation, sedimentation and redox processes. The coastal waters also are a highly dynamic transition zone, resulting in very diverse temporal and spatial chemical and biological changes. Total concentrations of iron in coastal waters though are generally several orders of magnitude higher than open ocean values and at a first glance, iron limitation of primary production in coastal areas seems not very likely. However, temporal growth limitation by iron can occur in some coastal upwelling regions (Bruland et al., 2001; Hutchins and Bruland, 1998) and fjord systems (Öztürk et al., 2002).

The world's largest estuary, the Baltic Sea, serves as an excellent large scale laboratory to study trace metal chemistry over a wide salinity gradient. Here the total iron concentration decreases by more than an order of magnitude from the low salinity north-east (Bothnian Bay), via the Bothnian Sea to its central part (Baltic Proper), thus forming a natural well defined iron concentration gradient for studying physicochemical speciation of iron and the role of iron for primary production at different total (unfiltered) iron concentrations (Gelting et al., 2009). The authors observed significant variations in the physicochemical speciation, including the iron isotopes, at high temporal resolution from the euphotic zone. Other large river systems such as the Columbia River and Mississippi also show large gradients in iron concentrations but also act as significant sources of Fe to coastal regions (Powell and Wilson-Finelli, 2003; Lohan and Bruland, 2006).

In addition to photochemical processes and organic complexation it is the cycling of iron between particles, colloids and the truly dissolved fraction (<1 kD), rather than the total concentration, that determines the bioavailability of iron in coastal surface water. The truly dissolved fraction can rapidly be consumed during bloom conditions if this fraction is small and exchange processes between particulate-colloidal matter and the truly dissolved fraction are slow. Hence, knowledge about distribution and cycling of iron between these phases in the coastal zone is fundamental for predictions about iron limitation for plankton growth, and is key to understanding iron export pathways to the open ocean. For the Baltic Sea, Gelting et al. (2009) show that iron in the <1 kDa fraction never reached critical low levels during summer phytoplankton bloom conditions. Further, Fe(II) is generally not considered as an abundant source of bioavailable iron due to its short residence time in oxygenated water. However, a relatively high standing concentration of Fe(II), large enough to cover the demand for iron by cyanobacteria in Baltic Sea waters, was observed by Breitbarth et al. (2009) in a study paralleling Gelting et al. (2009).

Measurements of the physicochemical speciation of iron in freshwater during the last five years suggest that iron transport in rivers is associated with two types of carrier phases (besides detrital particles), an oxyhydroxide phase with associated CDOM (chromophoric dissolved organic matter, mostly consisting of humic acids) and an organic carbon (fulvic) phase (e.g. Lyvén et al., 2003; Andersson et al., 2006). Much of this fulvic phase is present as small colloids and in the truly dissolved fraction (<1 kD). When these phases reach the saline coastal water substantial aggregation of the Fe-oxyhydroxide fraction with associated CDOM is observed, whereas iron associated to the fulvic fraction show little aggregation (Stolpe and Hassellöv, 2007) and survives the sequential sequestration from the water column during gradual mixing with seawater (Krachler et al., 2005). It is possible that this land-derived fraction can reach the open ocean, as indicated by recent data (Laglera and van den Berg, 2009). With fulvic acid as one important carrier mechanism for riverine Fe, the influence of this Fe source reaches further out to sea than previously expected. Tovar-Sanchez et al. (2006) for example, suggested based on metal composition, that riverine and not dust born material was the main source of trace metal accumulation in a diazotroph (*Trichodesmium* sp.) dwelling the surface waters of the subtropical and tropical North Atlantic Ocean.

Back at the river-seawater interface, Gerringa et al. (2007) argue that particularly the weak iron ligand groups (L_2) may impede the precipitation of Fe in the Scheldt Estuary upon mixing with seawater and that the strong ligand (L_1) generally observed in the open ocean, albeit also present, were insufficient in concentration. Powell and Wilson-Finelli (2003) though point out that the latter is of crucial importance for Fe transport in the Mississippi river plume. Likewise, Buck et al. (2007) demonstrated the predominant importance L_1 type ligands for Fe transport into the sea from the Columbia River and San Francisco Bay plumes. The stability constants of these strong L_1 ligands are very similar to those reported by

Laglera and van den Berg (2009) for Fe bound to fulvic acids, indicating the importance of these ligands in controlling the solubility of dissolved iron in riverine and coastal systems. Clearly, Fe speciation in estuarine and near-shore waters can not be addressed in a generalized manner and systems may differ depending on watershed characteristics (e.g., pristine versus anthropogenically impacted) as well as the level and type of riverine input (Öztürk and Bizsel, 2003; Krachler et al., 2005) (see Sect. 5 for colloidal matter).

Ingri et al. (2006) suggest that iron isotopes could be used to roughly identify the two major suspended fractions for iron in river water, the oxyhydroxides phase, which shows positive δ^{56} values, and the fulvic fraction that has a more negative signal. River water-seawater mixing experiments by Bergquist and Boyle (2006) showed that aggregated Fe was enriched in heavy isotopes. Hence, aggregation and sedimentation of the oxyhydroxide fraction during estuarine mixing should remove heavy isotopes from surface suspended matter, resulting in a more negative signal in the suspended phase, as indicated by field data from the River Lena freshwater plume (J. Ingri, personal communication, 2009). Cycling of iron in coastal areas appears to result in export of a negative iron isotope signal in the truly dissolved fraction, suggesting that open ocean water generally has a negative dissolved isotope iron signal thus explaining the negative δ^{56} value in ferromanganese crusts in the deep-sea. However, recent data indicate that bottom water in the open ocean has a positive δ^{56} value (Lacan et al., 2008), although it should be noted that the dataset is limited to one depth profile.

Iron isotope data from surface water in the Baltic Sea reveal systematic temporal variations in the Fe-isotope signal. For example, the δ^{56} value changed from -0.1 to $+0.25$‰ during a diatom spring-bloom resulting in subsequent sedimentation of iron with a negative isotope signal (Gelting et al., 2009). During the summer a relatively stable positive δ^{56} value was measured in suspended matter at different locations. This was likely due to a combination of river introduced aggregated oxyhydroxides and particulate iron formed from oxidation of dissolved Fe(II) in surface water. In this low salinity system, river introduced Fe-oxyhydroxides aggregate, but may not sediment in the river estuaries due to the lack of detrital sinking and flocculation processes and hence can spread far into the Baltic Sea (Gustafsson et al., 2000). This system is in sharp contrast to recently revised very rapid aggregation and sedimentation processes for direct river – seawater mixing (Nowostawska et al., 2008).

Recent advances suggest that iron isotope measurements have a large potential to provide new information on iron cycling and iron transport from coastal areas to the open ocean (de Jong et al., 2007). Fe/Ti or Fe/Al ratios close to average crust material do not necessarily indicate that the suspended phase mainly reflects detrital particles. Both positive and negative iron isotope values have been measured although the sample has a Fe/Ti or Fe/Al ratio close to average crust material. Furthermore, a δ^{56} value around zero does not necessarily mean that the sample consists of mainly detrital rock fragments, as it usually is a mixture of iron particles with positive and negative δ^{56} values (Gelting et al., 2009). Recommendations for future work thus consist of a focus on this field including continuing the characterization of the carrier phase for Fe across the salinity gradient and into the open ocean.

5 Colloidal iron and organic matter

Ten years ago the focus of Fe biogeochemistry was on dissolved (filterable) iron speciation and quite specific iron complexes. Once overlooked and neglected (Wells, 1998), progress has been made in understanding the nature and importance of organic colloidal material in seawater and coastal systems and challenged the simple discrimination into particulate and dissolved iron (0.45 or 0.2 µm filtered). Furthermore, dynamic exchange between larger iron particles, colloidal iron, and soluble iron (defined as passing either a 0.02 µm or a 1 kDa filter) also directs interest towards the particulate and soluble phase. The FeCycle study, a mesoscale SF6 tracer release experiment without iron perturbation in HNLC waters southeast of New Zealand (Boyd et al., 2005), showed that iron recycling rates due to biological iron uptake and regeneration exceeded input of new iron by 10-fold. Further, particulate Fe would undergo a transformation from lithogenic to biogenic iron during settling through the mixed layer. Rapid biological processing (bacterivory and herbivory, subsequent biological uptake) after dissolution of dust deposited iron hydroxides and presumably also photolysis of siderophore complexed Fe(III)-hydroxide (Borer et al., 2005) resulted in exchange from the lithogenic particulate phase via the soluble to the biogenic particulate phase (Frew et al., 2006; Strzepek et al., 2005; Maldonado et al., 2005). The rapid exchange with particulate iron phases provides new insight into iron cycling and export dynamics since the role of particulate iron in iron biogeochemistry appears more important than previously assumed. During the Gothenburg workshop however, the main center of attention was on colloidal iron and we therefore focus thereon hereafter.

Moran et al. (1996) measured iron, among other bioactive trace metals, in colloidal matter obtained by cross-flow filtration of seawater. The major proportion of the dissolved Fe in open ocean seawater (here defined as 0.4 µm filtered) was found to be in the colloidal form (here defined as >0.02 µm–0.4 µm) (Wu et al., 2001), with continuing debate about the bioavailability of this fraction. Chen and Wang (2001) showed that freshly precipitated colloids were available to phytoplankton but aging processes (15 days) reduced markedly their availability. Wang and Dei (2003) demonstrated that Fe availability from colloidal matter to cyanobacteria (*Synechococcus*, *Trichodesmium*) is largely dependent on the size and origin of the material, with the tendency of Fe bound to smaller colloids and biogenic colloidal

material derived from the same species being more available. The transfer from the soluble to the colloidal fraction appears rapid for iron in comparison to for example Zn, resulting in dynamic cycling including particle formation, and the drawdown of colloidal Fe indicated uptake by phytoplankton (Hurst and Bruland, 2007). Further, colloidal Fe is photoreactive and thus also contributes to the bioavailable pool of Fe(II) in surface waters (Barbeau, 2006; Fan, 2008).

Dissolved organic matter (DOM, which contains the colloidal fraction) in seawater has previously been considered to be old (∼6 KY) and refractory (Bauer et al., 1992). This refractory pool is also known to be rich in aromatic chromophoric material therefore often called chromophoric DOM (CDOM). However, in the last ten years the picture has changed somewhat and now it is believed that in addition to the refractory pool seawater DOM also consists of in situ biologically derived material, rich in proteic matter and sacharides and saccharide derivatives as building blocks (Aluwihare et al., 1997). In addition significant findings have been made to understand that fractions of marine DOM possess a gel forming character, including spontaneous assembling into microgels after filtration, where calcium bridging is shown to be important (Chin et al., 1998). In addition, new microscopy based techniques have shown that fibrillar type materials, hypothesized to consist of acid polysaccharides, are abundant in many open ocean regimes (Santschi et al., 1998). This marine gel phase can be an important transfer route from truly dissolved to particulate pool of matter (Verdugo et al., 2004). These findings in the dissolved fraction seem to link well to the marine snow formation of transparent exopolymeric particles (TEP), which are important for carbon export (Engel et al., 2004), although direct experimental evidence linking the fibrillar material to TEP and sedimentation has been lacking.

To what extent these processes and phase transfers in organic matter are controlling the physicochemical states and vertical distributions of iron and other trace elements has previously only been hypothesized. Stolpe and Hassellöv (2010) coupled Flow Field Flow Fractionation (FlFFF) with ICPMS, on-line "humic" fluorescence and UV-absorbance detectors, and subsamples for Atomic Force Microscopy (AFM) to fractionate and identify different colloidal size classes and associated trace metals during phytoplankton bloom events in a Fjord on the North Sea coast of Sweden. They found both seasonal and vertical variations in the colloidal size distributions for iron and other trace elements and could use these in order to explain the apparent iron solubility and vertical distribution to a large extent (Stolpe and Hassellöv, 2010). During the winter season colloidal size distribution for iron (and many other elements) were only appearing in the CDOM fraction (∼0.5–3 nm), while during the spring bloom and summer bloom in two consecutive seasons the colloidal size distributions for iron were shifting dramatically. In addition to the CDOM phase, iron partitioned into two larger size classes. With AFM these two colloidal populations were identified to be semispherical (3–7 nm) and fibrillar (∼0.5 nm thick and 30–200 nm long). From the partitioning of other elements and their size and shape it was hypothesized that the semispherical colloids were mainly thiol rich proteic biopolymers, while the fibrillar materials were polysaccharide rich exudates that could be the precursors of the microgels proposed by Chin et al. (1998). The conclusion that the seasonal variations of iron association with different colloidal phases to some extent control the apparent iron solubility in estuarine water is in line with the findings from Bergquist et al. (2007), implying that colloids in the open ocean control iron solubility. Likewise, Boehme and Wells (2006) and Floge and Wells (2007), using FlFFF coupled to excitation emission matrix spectroscopy and a UV-absorbance detector, observed a shift in colloidal size class distribution between protein-like and humic-like fluorescence of CDOM during phytoplankton blooms in an estuary.

Progress has been made in studying the behavior of iron oxide nanoparticles in different freshwater and salt matrixes and drawing conclusions for the inorganic phase within the filterable fraction (Hassellöv and von der Kammer, 2008, and references therein). Partly based on this work, the understanding of flocculation processes has improved and previous concepts (Sholkovitz, 1978; Sholkovitz et al., 1978) have been confirmed. Mylon et al. (2004) using natural organic matter (NOM) coated synthesized hematite colloids, show that the rate of colloid aggregation reaches a maximum at a salinity of 12, resulting in a removal of 80–90% of dissolved iron in a process occurring on a time scale of seconds (Nowostawska et al., 2008). The colloidal particles are stabilized by NOM due to electrostatic and repulsive forces (Mosley et al., 2003; Sander et al., 2004). Theoretically in seawater the conditions would favor attachment, but low particle concentrations result in a low collision frequency. Further, colloidal matter undergoes a transformation in size distribution and elemental composition upon introduction from fresh water into a seawater system (Stolpe and Hassellöv, 2007). The efficiency of transport through salinity gradients needs more investigation and isotope studies may be of significant importance to form a proper understanding of fluvial iron inputs into the sea (see Sect. 4).

As aforementioned, recent methodological advancements include the application of field flow fractionation (FFF), in conjunction with size fractionation by membrane and/or ultrafiltration techniques, to studies of the metal-colloidal phase (Boehme and Wells, 2006; Stolpe et al., 2005). FFF was generally applied to samples from coastal systems and detection limits necessitate the use of pre-concentration steps. While being a powerful tool to characterize size fractionated material, FFF can also help in developing robust filtering methods particularly at the lower end of the size range, as results reveal artefacts from membrane filtration can result in unintended removal of undersized material (Howell et al., 2006). The relevance of this for open ocean seawater

requires further testing. Further, cross-flow ultra-filters are defined as a molar cut-off, which may result in retention of undersized components and permeation of oversized components, as well as separation of size and chemical composition (Assemi et al., 2004). An intercalibration of cross-flow filtration techniques was carried out previously (Buesseler et al., 1996), but a new approach including classical membrane filtration and utilizing FlFFF coupled to ICPMS may yield valuable information about the robustness of different filter membranes with regard to fractionation of colloidal size classes and their elemental composition.

We conclude that future research directions should encompass further in depth characterizations of the different phases (particulate, colloidal, soluble), which may lead to a redefinition of the term dissolved iron. This will also lead to a better structural definition of bioavailable iron. We need to learn how iron is fractionated into specific size classes, what the exchange kinetics between these phases are, and what controls/catalyzes them. Specifically, the origin and nature of iron binding ligands needs to be further addressed to elucidate the role and characteristics of different ligand classes (L_1, L_2). In that, we may need to overcome measurement artifacts due to pre-concentration procedures that are necessitated due to the detection limits especially in open ocean applications (see also last two paragraphs of Sect. 6).

6 Linking biological processes to iron chemistry

Most areas of the open ocean have surface trace metal concentrations between picomolar and nanomolar levels, which are about one millionth of the concentration in phytoplankton cells (Morel and Price, 2003). Iron is required for many important cellular processes such as photosynthesis, respiration, nitrogen fixation and nitrate reduction. A recent laboratory study involving 15 neritic and oceanic phytoplankton species produced an elemental ratio of $C_{124}N_{16}P_1Fe_{0.0075}$ (Ho et al., 2003), similar to previous reviews of Fe:C ratios which have found a range of 2.3–370 µmol:mol (Sarthou et al., 2005; see also Twining et al., 2004). Research has linked the oxygenation of the oceans and the subsequent drop in iron solubility and thus iron availability to the evolution of more iron efficient phytoplankton (Quigg et al., 2003; Saito et al., 2003) that are able to cope with the low iron open ocean conditions. Phytoplankton species have evolved very effective acquisition mechanisms with high trace mtal affinities that involve interactions with organic iron binding ligands. Uncertainties remain on the nature of such ligands, which control Fe chemistry and bioavailability in marine systems (Hunter and Boyd, 2007).

Culture experiments have established that marine phyto- and bacterioplankton have different iron requirements that are linked to their biogeographical sources (Sunda and Huntsman, 1995; Brand et al., 1983). More recent work has shown that picophytoplankton, which dominate the oligotrophic regions of the oceans, are able to grow optimally in culture at extremely low inorganic iron concentrations of 10–15 pM inorganic Fe, (Timmermans et al., 2005). Our ability to relate these studies to the real environment is however limited by our understanding of the chemical speciation of iron in the ocean (Gledhill and van den Berg, 1994; Rue and Bruland, 1995). These studies indicated that dissolved iron is strongly complexed in the ocean, results which have been confirmed on many occasions since (as discussed in Hunter and Boyd, 2007). The composition of this organic fraction is still not well understood, although it appears likely that it will consist of autochthonous complexing ligands produced by marine phyto- and bacterioplankton (Mawji et al., 2008; Boye et al., 2005; Kondo et al., 2008; Vong et al., 2007) and complex organics such as humic/fulvic acids (Laglera and van den Berg, 2009). Calculations of the inorganic iron concentration based on measurements carried out by competitive equilibration cathodic stripping voltammetry show that inorganic iron concentrations in the ocean are of the order of 10^{-14}–10^{-11} M (Morel et al., 2008), although these calculations neglect the contribution of Fe(II), which may also be present at concentrations of the order of 10^{-11} M in surface waters (e.g. Hansard et al., 2009; Roy et al., 2008b; Croot et al., 2001). It is not clear how much of the organically complexed iron is available to marine phyto- and bacterioplankton, and parameters controlling Fe bioavailability to primary producers are still poorly understood.

Fe bioavailability is influenced by its chemical forms (speciation, redox state), biological cycling, and the different uptake strategies of the phyto- and bacterio-plankton communities (Barbeau et al., 1996; Hutchins et al., 1999a; Strzepek et al., 2005). Competition for available Fe is strongest when Fe is in short supply (e.g. Worms et al., 2006). Recent advances in our understanding and abilities to model iron uptake by marine phytoplankton (Morel et al., 2008; Shaked et al., 2005; Salmon et al., 2006) indicate that even at these low inorganic iron concentrations, open ocean phytoplankton will have sufficient iron to grow. Initially iron uptake was thought to be proportional to the concentration of inorganic Fe species (Fe') (Hudson and Morel, 1990). However, this model proved to be too simplistic to explain phytoplankton growth in natural systems where concentrations of inorganic iron species were extremely low due to organic complexation. Thus either the iron-ligand complex (FeL) is directly taken up, or the inorganic Fe availability is increased, e.g. by reduction to Fe(II). More recently two models have been published to describe the kinetics of Fe uptake. The Fe(II) model by Shaked et al. (2005) and the FeL model by Salmon et al. (2006). There are significant distinctions between these models which lead to differences in the predictions of phytoplankton iron limitation in culture experiments. While the Fe(II) model considers the surface Fe(II) concentration and explicitly includes unchelated Fe(III) as a source of Fe(II) for phytoplankton uptake, the FeL model considers the bulk concentration of Fe(II) in the

media as the controlling parameter and excludes unchelated Fe(III) as an irrelevant source (Morel et al., 2008). Morel et al. (2008) point out that the observed decrease in Fe uptake rates with increasing EDTA concentrations can only be explained by the Fe(II) model, which results in the conclusion that unchelated Fe(III) is indeed an important source of Fe(II) for phytoplankton uptake. However, phytoplankton species behave differently under Fe limitation and it is likely that future experiments under more natural conditions without the presence of EDTA will result in more realistic iterations of the iron uptake models. The role of other trace metals and organic material in the partly species specific adaptations of the iron acquisition system are not completely understood. As one example, Peers and Price (2006) have shown that copper is essential for electron transport in *T. oceanica* regardless of Fe status implying that selection pressure imposed by Fe limitation has resulted in the use of a Cu protein for photosynthesis in an oceanic diatom.

Adaptations to low iron environments have been found to include a reduction in cell size (Sarthou et al., 2005), changes in photosynthetic architecture (Strzepek and Harrison, 2004; Peers and Price, 2006) and substitution of iron containing proteins for non-iron containing proteins (Peers and Price, 2006; McKay et al., 1999). Further possible adaptations include the induction of high affinity uptake mechanisms such as the production of siderophores by marine prokaryotes (Vraspir and Butler, 2009) and uptake mechanisms that target specific iron containing compounds such as hemes (Hopkinson et al., 2008) or the production of iron storage proteins (Marchetti et al., 2009).

Microorganisms can exert a feedback effect on Fe chemistry, for example by releasing organic matter which is able to react with Fe (e.g. siderophores, exopolymeric substances (EPS), cell lysis material or fecal pellets), which can enhance iron bioavailability (e.g. Hutchins et al., 1999b). Heldal et al. (1996), for example, visualized and quantified metals bound to bacterial extracellular matrixes in applying X-ray transmission electron microscopy. The role of grazing as a source of organic, iron binding material via sloppy feeding and/or as a direct source of iron is often discussed. Several studies address this topic and a general consensus about the importance of grazing for iron recycling in surface seawater exists (Sato et al., 2007; Barbeau et al., 1996; Dalbec and Twining, 2009; Sarthou et al., 2008; Hutchins and Bruland, 1994; Hutchins et al., 1995; Tovar-Sanchez et al., 2007; Zhang and Wang, 2004). However, some results are inconsistent and the detailed mechanisms as well as the contribution of different grazer types such as protozoa, copepods, krill, and salps and their specific feeding mechanisms are poorly understood. Therefore, it is difficult today to estimate the overall function of grazing on the biogeochemical cycles of iron especially in HNLC regions.

Most marine microorganisms (bacterio- and phytoplankton) produce polysaccharides that are either stored as energy reserves or secreted as exopolymeric substances (EPS) (Schoemann et al., 2001; Decho, 1990; Hoagland et al., 1993). It has recently been shown that iron starvation is coupled to transparent expolymer particles (TEP) production in *Trichodesmium* (Berman-Frank et al., 2007). Recent studies also provide evidence that high concentrations of saccharides or carbon-rich organic matrices can enhance the growth of phytoplankton (Vasconcelos et al., 2002) and efficiently retain Fe (II) (Öztürk et al., 2004; Toner et al., 2009), a highly bioavailable form (Morel et al., 2008). Steigenberger et al. (2010) show that polysaccharides and cell exudates of *Phaeodactylum* sp. can also result in high hydrogen peroxide production, while the authors still observe a net stabilizing effect of Fe(II) potentially due to a combination of organic Fe(II) retention paralleled by superoxide production.

Hassler and Schoemann (2009) explore a Fe-related biogeochemical role for polysaccharides, by examining the influence of various organic ligands (siderophore, porphyrin, mono- and poly-saccharides) on iron solubility and its bioavailability to four keystone phytoplankton species of the Southern Ocean, representing different phytoplankton functional groups and size classes (*Phaeocystis* sp., *Chaetoceros* sp., *Fragilariopsis kerguelensis* and *Thalassiosira antarctica* Comber). Results show that saccharides can increase Fe uptake rates and Fe solubility above the level observed for inorganic Fe. Similar observations were made on natural plankton community from the Southern Ocean (Hassler et al., 2007). Given the ubiquitous presence of saccharides in the ocean, these compounds might represent an important factor to control the basal level of soluble and bioavailable Fe.

Over the past years, the Fe(II) pool has been recognized as an important source of bioavailable Fe and intermediate in Fe cycling. Albeit short-lived due to rapid re-oxidation to Fe(III), significant concentrations of Fe(II) were detected in different oceanic and coastal provinces (Breitbarth et al., 2009; Croot and Laan, 2002; Croot et al., 2008, 2005; Roy et al., 2008b; Hopkinson and Barbeau, 2007; Ussher et al., 2007). There has been emerging evidence that Fe(II) is retained in oxygenated water by organic ligands (Croot et al., 2001), which may be a product of marine biota (Roy et al., 2008b) or also of other origin and rain introduced (Willey et al., 2008). See Barbeau (2006) for a comprehensive review and also Sect. 7. The role of Fe(II) for phytoplankton nutrition and Fe(II) organic complexation provide interesting and relevant research topics for the near future.

Iron limitation also induces a decoupling in the use of macronutrients by phytoplankton, likely to influence the cycling of the major biogeochemical cycles (C, N, P, Si, S) over geological time scales (de Baar and La Roche, 2003). Further, light intensity can play an important role (Hoffmann et al., 2008; Maldonado et al., 1999; de Baar et al., 2005; Moore et al., 2007a and b). Moreover, Bucciarelli et al. (2010) examined the effect of Fe-light co-limitation on cellular silica, carbon and nitrogen in two marine diatom species, *Thalassiosira oceanica* and *Ditylum brightwellii*, observing a

1.4-fold increase in C:N ratio with a decrease in growth rate by 70% in both species and a decrease in biogenic silica per cell under severe Fe or Fe-light limitation. These results however are seemingly in contradiction with many previous lab and field studies showing increased diatom silicification under Fe limitation (Hutchins and Bruland, 1998; Takeda, 1998; Firme et al., 2003; Franck et al., 2003).

A significant contribution to the increasing knowledge on the interaction of biological processes with iron chemistry is made by the improvement of methods in this field. Intercalibrations of Fe detection methods were carried out and measurements of Fe are now possible in near real time in the field at picomolar level (Bowie et al., 2002, 2005, 2006; Johnson et al., 2007), including Fe(II) (Croot and Laan, 2002). More sophisticated shipboard incubation systems are available (Hare et al., 2007a; Hutchins et al., 2003; Pickell et al., 2009; Hare et al., 2005), allowing for more realistic experimental designs to assess Fe phytoplankton interactions. Methods were developed to detect cell surface Fe reduction and uptake (Shaked et al., 2004) and to measure cellular Fe (Hassler et al., 2004). New highly sensitive electrochemical methods have pushed our understanding of organic iron complexation in new directions (Croot and Johansson, 2000; Laglera and van den Berg, 2009). Utilization of laboratory based extensive instrumentation such as FlFFF, x-ray spectroscopy with TEM microscopy, as well as bioreporters, molecular techniques and genomic information allow for in depth studies and visualization of Fe limitation and Fe organic matter interactions (e.g. Heldal et al., 1996; Toner et al., 2009; Stolpe et al., 2005) and particularly also of iron bioavailability (Lam et al., 2006; Boyanapalli et al., 2007; Hassler et al., 2006).

Nevertheless, some methods still depend on high material/biomass concentrations and future development and work may lead towards more direct measurement techniques overcoming pre-concentration artifacts. The majority of phytoplankton iron interaction studies have been carried out invitro and with a limited range of species, and mostly did not include co-effects of other trace metals. Strong iron chelators such as EDTA and DFOB are commonly used to induce iron limitation in culture experiments and experiments are in part difficult to compare due to the variety and combination of factors (e.g. light intensity, temperature) applied. Thus, it is not clear how predominant the known low iron regime adaptations are in the oceanic environment. Albeit very challenging, future experiments should aim towards using more realistic media chemistries and natural biomass densities of cultures that were recently isolated. Methods and experiments need to be designed to link Fe chemistry to biological processes, including potential biological feedback mechanisms on Fe chemistry as also discussed with regard to climate change in Sect. 7. Further, our increasing ability to detect and characterize iron in seawater and in organisms (Mawji et al., 2008; Gledhill, 2007; Laglera and van den Berg, 2009; Vong et al., 2007) coupled to developments in techniques such as shotgun genomics (Rusch et al., 2007; Venter et al., 2004; Yooseph et al., 2007) and the potential of proteomics (Nunn and Timperman, 2007; Dupont et al., 2006) should lead to great advances over the coming years in our understanding of how organisms have adapted to low iron environments, and the implications of these adaptations to overall marine productivity and biodiversity. The development of in-situ measurement technology as for example suggested in the approach of Roy at al. (2008a), with the potential for deployment on moored sensor arrays, will greatly improve the spatial and temporal resolution of Fe measurements.

7 Iron and climate change

Global climate change will greatly influence atmospheric and hydrographic processes in the future. Most prominent features include changes in thermohaline circulation of the North Atlantic, warming of the polar regions, changing wind patterns resulting in reduced upwelling and wind driven mixing, as well as increased sea-surface temperatures and stratification (Boyd and Doney, 2003). Projected changes in relative humidity and land vegetation cover, affecting soil moisture and local dust availability, together with changed patterns in wind and precipitation, as well as riverine transport, will ultimately modify the iron supply to the open ocean (Boyd and Doney, 2003; Jickells et al., 2005). Further, rising atmospheric CO_2 acidifies the oceans, leading to changes in saturation state with respect to calcium carbonate and shifts the aragonite and calcite saturation depths (Feely et al., 2004) and potentially trace metal solubility. The abovementioned processes, albeit uncertainty over their magnitude and exact interrelations in the future exists, will affect marine biota, causing regime shifts, and modifications of biogeochemical cycling (Boyd and Doney, 2003). While climate change needs to be understood holistically, there is a need to evaluate regional and small scale physical, chemical, and biological processes in order to derive potential biogeochemical feedback mechanisms.

We here focus on direct local effects acting upon iron chemistry in seawater and primarily discuss the emerging field of trace metal biogeochemistry research encompassing two main areas, temperature shifts and changing seawater pH. Both temperature and pH are master variables for chemical and biological processes and effects on trace metal biogeochemistry may be multifaceted and complex. Ten years ago, this research field did not exist and data are scarce. Assessing the potential effects of sea-surface warming and ocean acidification on iron biogeochemistry is crucial and predictions to date are based on our understanding of the current ocean system. Despite the expanding knowledge and increasing awareness for trace metal chemistry in open ocean research during the past 20 years and the recently defined

field and intensifying work on ocean acidification research, there is yet little communication between these fields.

A decrease of the surface seawater pH from pre-industrial 8.25 to 7.85 within this century, and further by up to 0.7 units until 2300 is predicted (Caldeira and Wickett, 2003; Jacobson, 2005). In general, the H^+ ion concentration can directly affect metal uptake by phytoplankton via altered membrane transport activity or via direct competition of the H^+ ion with metal ions for membrane transporters or other metabolically active sites on the cell surface (Sunda and Huntsman, 1983; Vigenault and Campbell, 2005). Further main aspects are the inorganic solubility of iron, changes in organic complexation, phytoplankton – trace metal feedback mechanisms, and differences in redox chemistry.

$Fe(OH)_3$ solubility and Fe(III) inorganic speciation are expected to changed with ocean acidification (Liu and Millero, 2002, 1999). When seawater pH falls below 8, changes in the inorganic speciation result in an increase of the thermodynamic Fe(III) hydroxide solubility. Enhanced solubility above pH 7 in seawater of the warm or temperate ocean though is mainly due to organic ligands and suggests any change in solubility arising from acidification will be mainly related to the organic complexes (Liu and Millero, 2002). However, in cold water the solubility of Fe can exceed FeL concentrations (P. Croot, personal communication, 2009, calculated based on Liu and Millero, 2002), bringing inorganic speciation shifts due to pH and temperature back into the game. Interesting questions arise concerning whether ocean acidification could potentially also affect metal leaching from atmospheric deposits (see Sects. 2.1 and 2.2) and how the metastable colloidal Fe phase may be affected (see Sect. 5). The potential effect of pH acting directly on FeL complexes depends on the nature of Fe-binding functional groups. The H^+ stoichiometry of the Fe(III) binding sites defines the magnitude of acid dissociation constants (pK_a). Carboxyl groups have a $pK_a \sim 5$ and thus the conditional stability constant of the FeL complex ($\log K_{FeL}$) should remain unchanged above pH 6. In contrast, phenolic groups have a $pK_a \sim 9$ and $\log K_{FeL}$ will increase with pH (Sillen and Martell, 1971). Both groups can be found in siderophores. While to date no published experimental data on the pH effect for FeL can be found, Averyt et al. (2004) show a decrease of $\log K_{CuL}$ with lower pH in two lakes. Similar effects were observed for Cd ligands, but less so for Zn ligands (Sander et al., 2007). Further, iron chelates are more photolabile at lower pH (Sunda and Huntsman, 2003), which directly involves effects on Fe photochemistry (see below). Overall though, while FeL complexes may or may not be directly pH affected, alterations of organic iron complexation may still arise from biological ligand production processes, should those be affected by pH and/or temperature (see below). Several models of Fe uptake mechanisms for phytoplankton exist (Morel et al., 2008; Shaked et al., 2005; Salmon et al., 2006, see also Sect. 6) and their pH dependence may be largely connected on their reliance on Fe(II) as the actual species taken up and on the species capability to regulate pH at the cell surface.

It can be expected that pH driven changes in trace metal availability will trigger biological feedback mechanisms, which regulate trace metal availability to marine phytoplankton. These can be in form of exudates, cell lysates, or chlorophyll degradation products, and can serve as trace metal ligands to prevent toxic effects or to increase trace metal uptake rates. The capability of eukaryotic phytoplankton species to produce trace metal binding ligands either to prevent toxic effects or to increase uptake has been addressed (Ahner et al., 1997; Barbeau et al., 2001; Hutchins et al., 1999b). However, information on biological feedback mechanisms in response to climate change that affect trace metal chemistry is very limited. It should be noted that in contrast to the open ocean, estuaries and coastal areas might show a wide range in pH (5 to >9) (e.g. Chen and Durbin, 1994; Sunda and Huntsman, 1998) and obviously in temperature, to which phytoplankton species are adapted to. However, even considering that phytoplankton blooms may cause temporal increases in surface water pH due to CO_2 uptake, open ocean species are adapted to a very narrow range in pH. Further, some coastal areas such as the Oregon shelf temporarily experience subsurface input of low pH water and such systems could be valuable analogs for acidification and temperature effects in natural settings.

Several studies were carried out during the past years assessing changes in phytoplankton physiology using laboratory batch cultures and mesocosm pCO_2 perturbations. Changes in carbon and nitrogen fixation rates, calcification rates, and carbon export are reflective of pH effects on the biogeochemistry of the manipulated system (Riebesell et al., 2007; Orr et al., 2005, see also Biogeosciences Special Issue "The ocean in the high-CO_2 world II"), which unequivocally will also affect trace metal cycling. Further studies also reported combined effects of pCO_2 and temperature change (Hare et al., 2007b), and modeling studies also suggest potential interactions with irradiance effects due to changing stratification in the future ocean on phytoplankton physiology and species composition (Boyd and Doney, 2002). Seen in coherence with biological effects on organic Fe complexation, and in return again with Fe availability effects on phytoplankton, these studies indicate that phytoplankton physiology and species composition could exert biological feedback mechanisms on trace metal cycling as a function of pCO_2 and temperature in seawater.

Data from a coastal mesocosm CO_2 enrichment experiment (Breitbarth et al., 2010) suggest increasing dissolved iron concentrations with ocean acidification. The authors invoke a biological feedback mechanism at future seawater pCO_2 resulting in increased organic Fe(III) complexation, which requires further testing. More so, changes in Fe(II) chemistry were observed. In part, the underlying processes can theoretically be derived based on established relationships of Fe(II) oxidation rates and inorganic Fe(II)

speciation in presence of different oxidizers over environmentally relevant ranges in pH, temperature, and salinity (Santana-Casiano et al., 2006; Gonzalez-Davila et al., 2006; Santana-Casiano et al., 2005; Millero and Sotolongo, 1989; Millero et al., 1987; Croot and Laan, 2002). For example, over a seawater pH decrease of 0.5 units, a 10-fold increase in the half-life of Fe(II) can be expected and the effects of ocean acidification may thus override the influences from sea-surface temperature changes (Santana-Casiano et al., 2005). Fe(II) oxidation kinetics are seemingly affected by organic complexation (e.g. Croot et al., 2001; Rose, 2003; Roy et al., 2008b, see also Sect. 6). Fe(II) ligands may be biologically mediated and potential biological feedback mechanisms in the future could thus further complicate the picture, requiring focused research in this field. Moreover, changing light regimes are expected to affect photochemical cycling of Fe in sunlit surface waters (Boyd and Doney, 2002). Both, light intensity and the light spectrum penetrating the water will influence photochemical processes and this field requires further attention.

Similar to seawater pH, temperature effects have been rarely studied in coherence with trace metal biogeochemical measurements in open ocean systems. It has been standard to date to carry out measurements of organic iron complexation at room temperature, but temperature has profound effects on metal speciation and solubility. Further, Rose et al. (2009) demonstrate synergistic effects of temperature and iron additions on phytoplankton physiology and community dynamics in Ross Sea waters. Likewise, Fu et al. (2008) demonstrate that pCO_2 perturbations alone may not give the sole answer to potential physiological changes in phytoplankton, since these can be modified by interactions with Fe limitation. CO_2 and N_2 fixation rates in the future ocean may be controlled by a combination of Fe availability and pCO_2, further stressing the need to elucidate future changes in seawater iron chemistry.

Overall, climate change effects on iron speciation and biological limitation are likely not going to be driven by a single factor, and Rose et al. (2009) stress the importance of multivariate studies in order to understand ecosystem changes. It also remains to be shown how climate change may alter the interrelations of iron with other trace metals and macronutrients. For example, laboratory experiments showed that cadmium toxicity can be reduced under high iron availability, suggesting that cadmium is a competitive inhibitor of the iron uptake system or iron dependent cellular processes (Foster and Morel, 1982; Sunda and Huntsman, 2000). Similar observation are made for iron limited natural phytoplankton assemblages from the Southern Ocean by Cullen et al. (2003) who suggest that Fe limited phytoplankton take up more Cd resulting in lower $Cd:PO_4$ ratios in surface waters. Iron co-limitations and interactions with other nutrients and trace metals have been observed (e.g. Schulz et al., 2004; Mills et al., 2004; Wu et al., 2003; Wells et al., 2005) and apparently the composition of trace metals and macro nutrients greatly affect natural Fe fertilization efficiency (see Sect. 2.2). Moreover, Statham et al. (2008) recently addressed glacier meltwater input of iron and colloidal matter from the Greenland Ice Sheet. In the context of the expected changes for Fe biogeochemistry discussed here, their study illustrates how atmospheric warming can act on various levels, evidentially affecting iron biogeochemistry in the sea.

We conclude that ocean acidification may result in increased Fe(III) solubility, is likely to decrease stability of some FeL complexes, and is likely to increase Fe(II) stability. It may also change the mechanisms of Fe acquisition by cells, which though depends on the Fe status of the regime and the type of phytoplankton species present. Temperature effects may be smaller in comparison, with most pronounced changes though to be expected in polar waters. Recommendations for future research directions are systematic measurements of Fe(III) solubility in pH range 7–9 and effects of Fe-binding ligands along with the study of temperature effects thereon, and field experiments in upwelling regions with a focus on low pH regimes. Moreover, the role of organic ligands in enhancing Fe(II) stability needs to be investigated as well as effects of pH and temperature on the photoreactivity of Fe(III)L complexes. It is largely unknown what the pH controls in organisms are, and how they affect Fe acquisition. More emphasis is needed on measurements and control of the seawater carbonate system, including pH, in field studies and laboratory cultures. Protocols carried out to achieve pH control need to be reported and researchers are urged to report pH data on the total or seawater pH scale to ensure comparability of different studies. The comprehensive "Guide for Best Practices in Ocean Acidification Research and Data Reporting" was recently published and should be adapted for trace metal research (http://www.epoca-project.eu/index.php/Home/Guide-to-OA-Research/).

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